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INVESTIGATIONS OF EFFECT OF INTERSTITIAL IMPURITIES ON THE STRUCTURE AND PROPERTIES OF TUNGSTEN SINGLE CRYSTALS

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INVESTIGATION OF EFFECT OF INTERSTITIAL IMPURITIES ON THE STRUCTURE AND PROPERTIES OF TUNGSTEN SINGLE CRYSTALS

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The effect of individual interstitial impurities on the structure and properties of tungsten and the identification of the most harmful impurities are discussed, with reference to the low-temperature embrittlement of tungsten and production of high-grade structural materials. Studies on the effect of artificial saturation of tungsten single crystals with carbon, oxygen, and nitrogen showed that carburizing produced a sharp increase in disperse carbides responsible for the rise in carbon content, greater dislocation density leading to inhibition of dislocation migration and thus to microcracks, and higher 25°C yield point; oxygen saturation did not influence the plastic properties but produced high dislocation density at the grain centers; nitrogen treatment caused no changes in structure or mechanical properties and only rare formation of nitrides on the grain boundaries; hydrogen had the least influence on embrittlement.

The chief obstacle to using tungsten as a structural material is its lack of low-temperature plasticity, which is attributable mainly to the low solubility of interstitial impurities in the tungsten lattice (Bibl.1). Even if only minute amounts of these impurities (of the order of 0.0001%) are present, they

* Numbers in the margin indicate pagination in the original foreign text.

form metalloid compounds with the tungsten (carbides, oxides, nitrides) which, being unfavorably located in the lattice and at the grain boundary, cause embrittlement of the tungsten.

Various studies performed in this country and abroad established that enhancing the degree of purity of tungsten, especially with respect to interstitial impurities, causes an improvement in its low-temperature plasticity and is the most effective method of generally improving the plastic properties of tungsten. However, the literature contains practically no studies on the effect of individual interstitial impurities on the structure and properties of tungsten. Thus, it remains unclear exactly which one of the interstitial impurities has the greatest influence on the ductile-to-brittle transition temperature of tungsten; this is a prerequisite for a better understanding of the physical nature of the embrittlement of tungsten during cooling and for developing a process for the production of high-grade structural material.

The present investigation was intended to determine the effect of the saturation of tungsten with carbon, oxygen, and nitrogen on the structure and mechanical properties of this metal (tungsten does not interact with hydrogen). Single crystals are an indispensable starting material for such investigations, since one can thus eliminate the effect of grain boundaries as well as the attendant errors in the experimental findings and conclusions in certain cases. Single crystals of tungsten, measuring 4 mm in diameter and 250 mm in length, were grown by electron-beam zone melting (Bibl.2) in a vacuum of 5×10^{-5} mm Hg, at a zone traveling rate of ~5 mm/min. The number of passages was two. The starting material used was extremely pure (99.99%) cast tungsten, previously subjected to a special hydrogen-removal treatment. The amounts of interstitial impurities in the grown single crystals were found to be: C = 0.0012% (determined by the combustion method); O_2 = 0.001% and N_2 = 0.001% (determined by vacuum melting). All analyses were performed at the Analytic Laboratory of the A.A.Baykov Institute of Metallurgy. The purity of the single crystal was checked by measuring the ratio of electric resistance at 300°K to the electric resistance at 4.2°K which, for the obtained single crystals, was 11,200. With the aim of eliminating the effect of crystallographic orientation on their /85 mechanical properties, all single crystals were grown with the same crystallographic orientation, by means of a special batch. The longitudinal orientation of the crystal axis was: 14° from [011] and 29° from [111].

The specimens for artificial saturation consisted of previously prepared discontinuous monocrystalline microspecimens with a test section 15 mm in length and 1.8 mm in diameter [made of tungsten single crystals, electrolytically polished by a method similar to that by Strat (Bibl.3)]. Carburizing was carried out by case-hardening in graphite under heating in a vacuum furnace (vacuum 2×10^{-6} mm Hg) at 1300°C for 6 hrs. The specimens and graphite powder were placed in a tungsten boat, thus eliminating any chance contact between the coating and possible metal impurities. After coating, the specimens were subjected to homogenizing vacuum annealing at ~2000°C for 8 hrs.

Saturation with oxygen was accomplished by placing the specimens, together with high-purity tungsten trioxide, in an evacuated soldered quartz ampoule which was kept at 1200°C for 48 hrs. The weight ratio of WO_3 to the specimen was 3:1. Saturation with nitrogen was performed during induction heating of the specimens in an atmosphere of high-purity nitrogen (99.99%) at ~2300°C for 5 hrs. The results of chemical analysis, measurements of electric resistance at 25°C, $K = \frac{\rho 300^\circ K}{\rho 4.2^\circ K}$, and the saturation regimes are presented in Table 1.

For mechanical tests and determination of the transition point to the

TABLE 1

CONDITIONS FOR CONTROLLED DOSAGE OF INTERSTITIAL IMPURITIES AND RESULTS OF ANALYSIS*

Impurity	Temperature °C	Saturation Time, hrs	Amount in %	ρ 25° C, μohm-cm	$K = \frac{\rho 300\,°K}{\rho 4.2\,°K}$
C	1300	6	0.054	5.4	220
O_2	1200	48	0.002	4.8	12000
N_2	2300	5	0.001	4.8	11000

* The K ratios were determined at the Faculty for Low-Temperature Physics, Moscow State University.

brittle state, the specimens, after saturation, were electrolytically reduced in thickness (only the test section) from 1.8 to 1.1 mm in diameter. This ensured complete removal of the defective surface layer. Tensile tests were performed in a Shevenar type tensile microtesting machine at room temperature and at a strain rate of 0.5 mm/min, with recording of the strain diagrams on photographic plate. In calculating the critical shear stress, it was observed that the primary slip system in tungsten is the system $\{110\}$ $\langle 111 \rangle$ (Bibl.4). The transition point to the brittle state was determined from static bending tests of microdiscontinuous specimens over a measured interval of transition temperatures. The transition point was taken as the temperature below which the specimens failed on bending through 90°. The averaged results of mechanical tests on 2 - 3 specimens, microhardness (under a load of 100 gm), and transition point are presented in Table 2.

Table 2 indicates that tungsten single crystals are fairly easy to impregnate with carbon. Over 6 hrs of carburizing at 1300°C, the amount of carbon increased from 0.0012% to 0.054%, i.e., nearly 45 times. After this, the K ratio decreased sharply, from 11,200 to 220. Since the change in electric resistance at 25°C, following saturation with carbon was insignificant, the decrease in the K ratio took place at the expense of an increase in the residual

TABLE 2 /86

MECHANICAL PROPERTIES OF TUNGSTEN SINGLE CRYSTALS AT 25°C AND RATE OF ELONGATION OF 0.5 mm/min

Status of Specimen	$\sigma_{0.2}$, kg/mm²	τ_{cr}, kg/mm²	σ_B, kg/mm²	δ, %	ψ, %	H_μ, kg/mm²	Transition Temp. °C
After 2 passages	33.8	15.7	102	10	100	310	below —196
2 passages + saturation with C	73	34.1	83.5	8	40	351	0
2 passages + saturation with O_2	31.3	14.5	90	10	100	310	below —196
2 passages + saturation with N_2	32.8	15	93.5	10	100	310	»

electric resistance of the tungsten single crystal at 4.2°K. This is confirmed by chemical analysis, which points to a marked increase in the amount of carbon following the carburizing of the single crystal. Unfortunately, it is impossible at present to determine the quantitative ratio of the amount of carbon in the tungsten to its electric resistivity at 4.2°K. However, there is no doubt that such a relationship exists. Earlier (Bibl.5), we showed by electron microscopy that carbon in tungsten single crystals is present as the carbide W_2C. Considering the low solubility of carbon in the tungsten lattice, it may be stated that the increase in the carbon content following carburizing is due to the formation of the carbide W_2C rather than to the solution of carbon in the tungsten. In fact, a microstructural analysis indicates a sharp increase in the amount of impregnating carbides. The carbides are highly disperse and their distribution over the structure is uniform (Fig.1).

The dislocation density in tungsten single crystals, following their saturation with carbon, increases by nearly one order, namely, from 1.2 ×

$\times 10^6$ disl./cm^2 to 1×10^7 disl./cm^2 (Figs.2, 3). The increase in dislocation density may have to do with the staining of existing dislocations by carbon, /87 i.e., it could be reasoned that the increase in the amount of carbon leads not

Fig.1 Carbides in Tungsten Single Crystal after Carburizing
Electropolishing in 2% NaOH × 600

Fig.2 Dislocations in Initial Tungsten Single Crystal Prior to Carburizing
Electropolishing in 2% NaOH, × 800

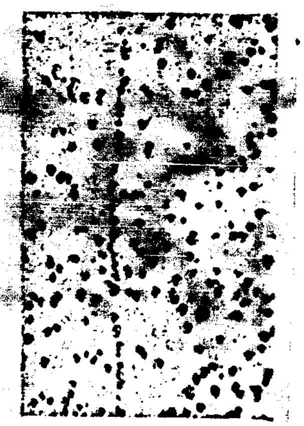

Fig.3 Dislocations in Tungsten Single Crystal after Carburizing
Electropolishing and electrolytic etching in 2% NaOH, × 800

so much to an actual rise in dislocation density as to the detection, during electrolytic etching, of "pure" dislocations present in the initial single crystals but not previously detected. However, chemical etching with Wolf's reagent (Bibl.6), where no staining effect is involved, produces absolutely the same results. Hence, it must be considered that the carburizing of tungsten single crystals leads to the formation of new dislocations, meaning that the interstitial carbon present in the form of the carbide W_2C in the tungsten lattice, with its crystallographic structure differing from that of tungsten, generates internal stresses whose relaxation leads to the formation of dislocations.

The increase in carbon content also sharply affects the mechanical properties of the single crystal. The critical shear stress and yield point at 25°C increase by a factor of more than 2, from 15.7 to 34.1 kg/mm^2 and from 34 to 73 kg/mm^2, respectively. The hardness increases somewhat, while the plastic properties decrease. The relative reduction in area decreases from 100 to 40% and the transition point to the brittle state increases to 0°C. The microspecimens prior to carburizing withstood bending through 90° at the temperature of liquid nitrogen. The stress-strain diagram of the specimens of tungsten single crystals, following their carburizing, is quite interesting (Fig.4, Curve 3).

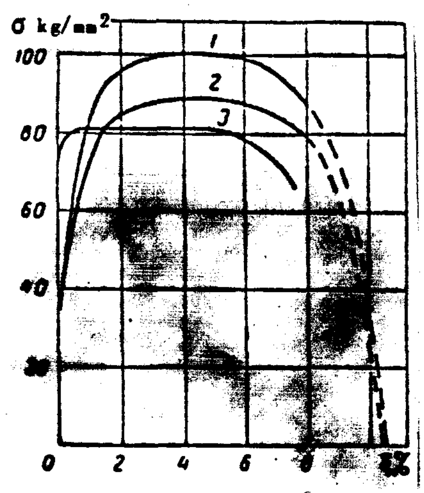

Fig.4 Strain Curves of Specimens of Tungsten Single Crystals
1 - Initial single crystal; 2 - After saturation with oxygen; 3 - After saturation with carbon.

The yield point, having more than doubled, approaches the ultimate strength. Noteworthy is the virtually insignificant rate of strain hardening compared with the initial pure single crystal. The ultimate strength after carburizing is roughly 20% lower than the ultimate strength of the pure single crystal. Such a behavior of the crystal on elongation, following its carburizing, is primarily due to an increase in the amount of disperse carbides. It is known that, in the presence of a second phase, the initial plastic flow is a function of the distance between the second-phase particles. Therefore, the sharp increase in critical shear stress and yield point as well as the limited increase in hardness are directly linked with the amount of carbides present. The low strain hardening rate is apparently connected with the appearance of numerous dislocation sources. It appears that, in the presence of a large number of carbides, plastic deformation proceeds chiefly owing to a multiplication of dislocations. Migration of the dislocations takes place over small distances, resulting in a weakening of the effect of all kinds of hardening mechanisms of the dislocation type.

It could well be that the decrease in strain hardening rate is due to the increase in the role of transverse slip, inherent in metals with body-centered cubic lattice. In the presence of a large number of obstacles formed by disperse carbides, screw dislocations might circumvent these obstacles by migrating to the adjacent slip planes, which would logically lead to a change in the /88
hardening mechanism. In the absence of strain hardening, it is natural for the strength to decrease as well. If there is a large number of obstacles to the migration of dislocations as well as a large number of dislocation sources, conditions become favorable for the formation of a microcrack - the origin of brittle fracture. The plastic properties of the single crystal deteriorate: The relative reduction in area decreases, while the temperature of transition to the brittle state increases.

As can be seen from Table 1, saturation with oxygen at 1200°C causes practically no increase in the oxygen content of the tungsten. What is more, the accompanying definite increase in the K ratio gives reason to believe that exposure of tungsten to an oxygen-containing atmosphere leads to some elimination of carbon from the tungsten. Microstructural analyses revealed no appreciable changes in the quality of the carbides or in the dislocation density, although a tendency toward a decrease in dislocation density and amount of carbides in the peripheral sectors of the specimens was observed. The critical shear stress somewhat decreased (by 2.5 kg/mm^2), while the plastic properties

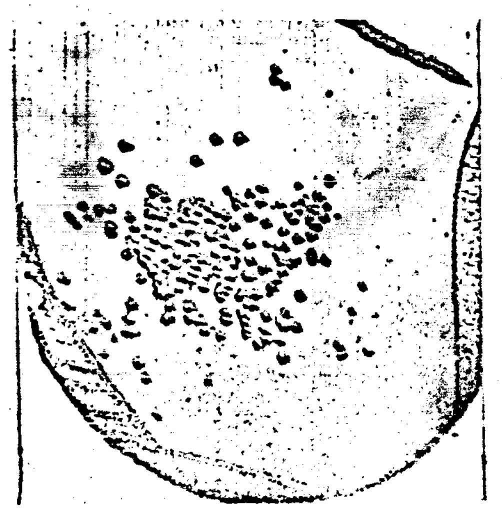

Fig.5 Microstructure of Polycrystalline Tungsten after High-Temperature Saturation with Oxygen
Electropolishing and electrolytic etching in 2% NaOH, × 1000

remained unchanged. The strength dropped slightly, which must be attributed to the appearance of a small number of micropores in the specimens, as revealed by metallographic examination. It seems that the formation of such pores is associated with the formation of CO during interaction between oxygen and the tungsten carbides. The slope of the strain curve remained unchanged. The fact that oxygen purifies tungsten of carbon has been confirmed by exposing cast polycrystalline tungsten containing 0.03% carbon to an atmosphere of helium plus a small amount of oxygen (~0.02%), at 3000°C for 15 hrs. The carbon content of the tungsten after such treatment decreased by ~0.005%.

Figure 5 presents the microstructure of tungsten after decarburizing. No dislocations can be seen in the regions adjoining the grain boundaries, while the dislocation density at the grain center is very high. The grain boundaries represent microcracks and large pores can be observed in certain places. All this points to the decarburization of tungsten by the reaction $2W_2C + O_2 = 2CO + 4W$. It is interesting that grains containing no dislocations at all are observable at the specimen periphery. Thus, it may be concluded that the density of dislocations in undeformed tungsten is directly connected with the amount of carbon. The elimination of carbides from tungsten weakens the dislocations and enables them to migrate and become obliterated. As is known, prolonged homogenizing annealing is not performed until the dislocation density of tungsten decreases; this may be directly attributed to the strong hardening effect of carbides on tungsten.

Saturation with nitrogen caused no changes in the structure or mechanical properties. Despite existing literature data pointing to the existence of /89 tungsten nitrides, no such nitrides could be detected in the structure. Apparently, such nitrides may form only at the surface or at grain boundaries, but - like the oxides - do not form within the tungsten lattice. It may be that this has to do with the considerable difference between the atomic diameters of oxides and nitrides and the atomic diameter of tungsten.

Thus, carbon produces the greatest impairment of the properties, particularly of plasticity and structure. Oxygen and nitrogen do not affect the properties of tungsten single crystals; in the case of polycrystalline tungsten, however, the possibility of the formation of oxides and nitrides along the grain boundaries and of a possible concomitant intercrystalline embrittlement cannot be ignored.

Conclusions

1. An increase in the carbon content of tungsten single crystals from

0.0012 to 0.054% causes a sharp decrease in the ratio between electric resistivity at 300°K and at 4.2°K (from 11,200 to 220). The number of carbides in the structure rises. The dislocation density increases by nearly one order, namely, from 1.2×10^6 to 1×10^7 disl./cm^2. The critical shear stress and yield point increase by a factor of more than 2. The relative reduction in area decreases from 100 to 40%. The ductile-to-brittle transition temperature rises from less than -196 to 0°C. The dislocation density in undeformed tungsten is directly related to its carbon content. A decrease in carbon content causes a reduction in dislocation density.

2. Saturation with oxygen and nitrogen causes no appreciable increase in their content in tungsten single crystals. It seems that oxygen and nitrogen do not significantly affect the structure and mechanical properties of these crystals.

Thus, our findings indicate that, with respect to the degree to which they influence the ductile-to-brittle transition point, interstitial impurities may be classified in the following tungsten-embrittling sequence: carbon, oxygen, nitrogen, hydrogen (the least effect of all). Of the other metals of Group VIA, chromium apparently is affected in a similar manner by this sequence (Bibl.7). A special investigation of the effect of carbon on molybdenum will have to be performed. It is interesting that for metals of Group VA, the sequence of increasing effect of embrittling interstitial impurities is exactly reversed - hydrogen, nitrogen, oxygen, carbon (Bibl.1).

<u>Resumé</u> /90

As is known, interstitial impurities sharply deteriorate the plastic properties of tungsten (Bibl.1). The literature, however, contains almost no

studies of the effect of the individual interstitial impurities on the structure and properties of tungsten and the identification of the most harmful of these impurities. Nevertheless, this knowledge is necessary for a fuller understanding of the physical nature of the low-temperature embrittlement of tungsten, as well as for development of techniques for the production of high-grade material. The present investigation was intended to investigate the effect of the artificial saturation of tungsten single crystals with carbon, oxygen, and nitrogen on the structure and mechanical properties of the crystals.

Single crystals of tungsten, 4 mm in diameter and 250 mm in length, were grown by electron-beam zone melting in a vacuum of 5×10^{-5} mm Hg at a zone travel rate of 5 mm/min (Bibl.2). The number of passages was two. The content of interstitial impurities in the grown crystals was found to be: C = 0.0012% (determined by the combustion method); O_2 = 0.001% and N_2 = 0.001% (oxygen and nitrogen were determined by vacuum melting). The ratio of the electric resistivity of the single crystals at 300°K and 4.2°K was found to average 11,200. All single crystals had the same crystallographic orientation of the longitudinal axis (14° from [011] and 29° from [111]), accomplished with the aid of a special batch. The specimens for saturation were prepared from single crystals, electrolytically polished by a method similar to that by Strat (Bibl.3) and had the form of discontinuous microspecimens with a test section 15 mm in length and 1.8 mm in diameter. Saturation with carbon was accomplished by the case-hardening process in graphite, with heating in a vacuum furnace (vacuum $2 \times \times 10^{-6}$ mm Hg) at 1300°C for 6 hrs. After saturation, the specimens were subjected to homogenizing vacuum annealing at ~2000°C for 8 hrs.

For saturation with oxygen, the specimens, together with high-purity tungsten trioxide, were placed in an evacuated soldered ampoule and kept at

1200°C for 48 hrs. Saturation with nitrogen was performed during the induction heating of the specimens in an atmosphere of high-purity nitrogen at ~2300°C for 5 hrs.

The results of chemical analysis, measurements of electric resistivity, and saturation regimes are presented in Table 1.

For mechanical tests and determination of the transition point to the brittle state, the test section of the specimens was electrolytically reduced in diameter from 1.8 to 1.1 mm. Tensile tests were performed in a Shevenar type tensile microtesting machine at 25°C and at a strain rate of 0.5 mm/min.

Tungsten single crystals become carburized fairly rapidly. In six hours of carburization at 1300°C, the carbon content increases from 0.0012 to 0.054%, i.e., nearly 45 times. The K ratio drops sharply from 11,200 to 220. It follows from another paper (Bibl.5) that carbon is present in tungsten in the form of the carbide W_2C and hence, considering the low solubility of carbon in the tungsten lattice, it must be assumed that the increase in carbon content occurs as a result of the formation of carbides.

Microstructural analysis actually does show a sharp increase in the amount of disperse carbides (Fig.1). The dislocation density in tungsten single crystals after carburizing increases by nearly one order - from 1.2×10^6 cm^{-2} to 1×10^7 cm^{-2} (Figs.2, 3). The increase in dislocation density must be related to a relaxation of the internal stresses set up when the hexagonal carbide W_2C enters the cubic lattice of tungsten. The critical shear stress and yield point at 25°C after carburizing increase by more than a factor of 2, namely, from 15.7 to 34.1 kg/mm^2 and from 34 to 73 kg/mm^2, respectively. The hardness increases somewhat, while the relative reduction in area decreases from 100 to 40%. The temperature of transition to the brittle state rises from -196° to

$0^{\circ}C$. Carburizing alters the shape of the strain curve of the single crystals: The yield point closely approaches the ultimate strength and the strain hardening almost disappears (Fig.4). Apparently, this is due to the appearance of a large number of dislocation sources (carbides) in whose presence plastic deformation proceeds chiefly owing to the multiplication of dislocations. The existence of a large number of dislocation sources and obstacles to the migration of dislocations (carbides) creates favorable conditions for the appearance of microcracks and thus the onset of brittle fracture. Thus, the plastic properties deteriorate as a result of carburizing.

Saturation with oxygen at $1200^{\circ}C$ causes practically no increase in the oxygen content of tungsten. The critical shear stress decreases somewhat (by 2.5 kg/mm^2) and the K ratio increases from 11,200 to 12,000. The plastic properties of the single crystals and the slope of the strain curve do not change. This suggests that oxygen not only fails to influence the plastic properties of tungsten single crystals but also removes carbon from them, as has been confirmed by the high-temperature oxygen saturation of cast polycrystalline tungsten during its heating in an atmosphere of helium containing a small amount of oxygen (0.02%) at $3000^{\circ}C$ for 15 hrs (Fig.5). Following the high-temperature oxygen saturation of tungsten, no dislocations are observed /91
in the regions adjoining the grain boundaries, whereas, on the other hand, the dislocation density at the grain centers is considerable. Grains containing no dislocations at all are observed at the periphery of the specimen. The grain boundaries represent microcracks, with gas-filled pores at some areas. This points to a decarburization of tungsten by the reaction $2W_2C + O_2 = 2CO + 4W$. Moreover, it may be concluded that the density of dislocation in undeformed tungsten is a direct consequence of its carbon content. The elimination of

tungsten carbides weakens the dislocations and enables them to migrate and become annihilated.

Saturation with nitrogen causes no changes in the structure or in the mechanical properties. We were unable to detect nitrides in the single crystal structure after saturation with nitrogen. Apparently, if such nitrides form at all, they will do so - like oxides - only at the surface or at the grain boundaries. Thus, it is carbon that exerts the most detrimental effect on the structure and properties of tungsten single crystals. These findings indicate that interstitial impurities may be grouped in the following "embrittling sequence" according to the degree of their influence on the transition point of tungsten to the brittle state: carbon, oxygen, nitrogen, hydrogen (least influence of all).

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